ASPECTS OF THE CHEMICAL AND RETORTING PROPERTIES
OF SELECTED AUSTRALIAN OIL SHALES

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INTRODUCTION

Much of the present understanding of the chemical processes occurring during the heating and retorting of oil shales is based on work carried out with shales from the American Green River deposit (1-3). However, this shale is not typical of oil shales found in other deposits, and comparative studies of the chemical properties and retorting chemistry of a variety of shales might provide further insights into the undoubtedly very complex chemistry of these materials.

This paper presents results of some laboratory scale studies of the chemical and retorting properties of representative samples from five Australian oil shale deposits. In general terms, the results obtained indicate that these shales differ significantly in their chemical properties both from each other and from the shale of the Green River deposit.

EXPERIMENTAL

The kinetics of the oil and gas formation during the retorting of the shales were determined using an apparatus essentially identical to that described by Campbell et al. (2). Heating rates of 3°C/min were used and the argon carrier gas flow rates were 130 cc/min for the determination of the oil formation, and 30 cc/min for the determination of the rates of gas evolution. The shale samples used in these studies were sized, and dried at 120°C for 12 hours prior to use.

Demineralization of the shale was carried out using HCl/HF digestion on ~90 μm sized samples. Solvent extraction studies on the demineralized shale were carried out using conventional soxhlet extractors. TGA studies were carried out using a computer controlled Cahn thermobalance (Model No. RG2050) of conventional design.

RESULTS AND DISCUSSION

The samples of shale used in this work all originated in the various shale deposits located near the coastal areas of central Queensland. These deposits are believed to be of tertiary age and of lacustrine origin, and in contrast to the Green River deposit contain only small amounts of mineral carbonates. As summarized in Table I, the chemical composition of these shales differ widely, ranging from the Nagoorin carbonaceous shale with an organic carbon content of 65%, to the more conventional Duaringa shale with an organic carbon content of 11%. The precise origin and nature of the black or carbonaceous shales found in the Nagoorin and Condor deposits are not understood at present, but from a chemical viewpoint significant differences between the black and conventional shales are readily apparent. Thus, the black shales are generally characterized by a high kerogen content, a significantly lower H/C ratio and a markedly lower oil yield per unit kerogen content. As will be shown below, the kinetics of the gas evolution from the black shales also differ from those of the normal shales.

The results of extraction of the kerogens isolated from the Stuart and Nagoorin shales with solvents of increasing polarity (Table II) indicate that these kerogens contain significant proportions of relatively low molecular weight, and presumably polar compounds. The fraction of kerogen extractable with a given solvent appears to be comparable with the results of similar studies on the Green River kerogen (4) and indeed with those obtained for bituminous coals (5,6). The appearance of the extract ranged from pale waxes for the less polar solvents to black, lustrous solids for pyridine, dimethyl formamide and dimethyl sulfoxide. The nature of extracts are not known at present, but elemental analysis on the dimethyl sulfoxide extracts showed these to have a lower H/C and higher O/C, S/C and N/C ratios than the original kerogen. This result would suggest that these extracts are composed of heteroatom-containing aromatic compounds. This very tentative conclusion

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is supported by TGA results which showed that the pyrolysis of the extracts results in a significantly higher proportion of involatile residues when compared to the original kerogen.

TABLE I

PROPERTIES OF OIL SHALES

Sample	Fischer Assay (Litres/ Tonne)	Assay[a] %C	%H	%N	%S	%O	H/C	Kerogen Content (wt %)	Ash in Kerogen (wt %)	Oil Yield/ g Kerogen (cc/g)
Nagoorin Carbonaceous (16998C)	232	65.2	4.94	2.74	0.1	17.9	0.91	72	0.2	0.32
Condor Carbonaceous (13338C)	69	28.3	2.43	1.29	0.4	11.0	1.03	33	0.4	0.21
Condor (19541C)	93	12.3	1.59	0.66	0.7	8.5	1.55	12	3.9	0.75
Stuart (18313C)	178	19.3	2.20	0.52	3.1	12.3	1.38	25	0.3	0.72
Duaringa (5363C)	86	11.0	1.93	0.40	0.1	8.3	2.09	14	4.7	0.61

(a) Based on shale dried at 120°C for 12 hours.

TABLE II

EFFECT OF SOLVENT POLARITY ON THE EXTRACTION OF KEROGEN

Solvent	% Kerogen Extracted Stuart	Nagoorin
Hexane	2.4	2.0
Acetone	4.4	5.8
Chloroform	6.0	6.2
Methanol	7.9	3.2
Pyridine	9.9	16.4
Dimethylformamide	19.5	25.6
Dimethylsulfoxide	27.2	30.2

The retorting properties of the various oil shales heated at a linear rate of 3°C/min in an inert gas atmosphere are summarized in Table III. The most notable features of these data are firstly the relatively high water content of these shales, particularly for the two carbonaceous shales, and secondly the poor oil yield (relative to the Fischer assay) obtained by this technique. This latter effect appears to be related to the heating rate, and recent work (7) has shown that at a heating rate of 15°C/min, an oil yield equivalent to the Fischer assay can be obtained for the Condor (19541C) shale. In this respect, the shales studied in the present work appear to differ significantly from the Green River shale, for which it has been shown (8,9) that the oil yields decrease significantly only at heating rates below 1°C/min. It is possible therefore that the much greater effect observed for the present shales is a reflection of the greater tendency of the oil produced to undergo coking reactions.

Typical results of kinetic studies on the rates of oil formation from various shales (Figure 1, Table IV) show some differences in kinetic behavior amongst the various shales, although the general appearance of the curves and the temperatures at which the oil yields are maximum are similar to those reported for the Green River Shale (2). The results of the least squares analysis of these data in terms of the Anthony-Howard model (3,10) for non-isothermal kinetics (Table IV) showed that the results of the Nagoorin, Condor, Stuart and Duaringa shales could be reproduced quite well by a single process with activation energies in the range 200-232 kJ mol^{-1} and relatively small (∿0-5 kJ mol^{-1}) standard deviation parameters. By comparison, the activation energy for the evolution of oil from the Green River shale heated at 2°C/min has been determined (3) as 219 kJ mol^{-1}. Only in the case of the Condor Carbonaceous shale was it necessary to consider two distinct processes

for the oil formation, in which the first process was responsible for 54% of the total oil yield and the second process for the remainder.

TABLE III

SUMMARY OF RETORTING CHARACTERISTICS[a]

Sample	Fischer Assay Litres/Tonne	Wt Loss on Drying (b) %	Oil %	Water %	Char %	Gas + Losses %	Oil Yield (% of Fischer Assay)
Nagoorin Carbonaceous 16998C	232	20.1	12.8	9.7	62.4	15.1	62
Condor Carbonaceous 13338C	69	14.3	6.1	8.0	79.9	6.0	99
Condor 19541C	93	3.4	6.0	3.8	82.3	7.9	75
Stuart 18313C	179	6.2	12.7	4.7	75.9	6.7	85
Duaringa 5363C	86	10.3	5.5	2.9	83.6	8.0	73

(a) Heating rate of 3°C/min in helium flowing at 130 cc/min. Particle size: – -3.3 mm + 1.4 mm
(b) Samples dried at 120°C for 12 hours
(c) Expressed as % of weight of dried shale.

TABLE IV

SUMMARY OF ACTIVATION PARAMETERS FOR OIL FORMATION[a]

Sample	Preexponential Factor		Activation Energy kJ Mole^{-1}	o (b) kJ Mole^{-1}	(°C) Temperature at which rate of oil formation is maximum
Nagoorin Carbonaceous (16998C)		2.5×10^{12}	201	5.1	420
Condor Carbonaceous (13338C)	Process (1)	1×10^{12}	195	1.0	420
	(2)	1×10^{12}	206	8.0	480
Condor (19541C)		1.0×10^{14}	232	0.05	455
Stuart (18313C)		1×10^{13}	215	5.0	445
Duaringa (5363C)		1×10^{14}	225	5.0	430

(a) Heating rate of 3°C/min, carrier gas flow rate of 130 cc/min. Values determined by least squares fit of data to Equation 1.
(b) Standard deviation of activation energies.

The effects of temperature on the rates of hydrogen, methane, carbon monoxide and carbon dioxide evolution from the five oil shales are shown in Figures 2-6, the integrated gas yields summarized in Table V, and the activation parameters for various representative contributing processes determined by analysis of the data in terms of the Anthony–Howard equation compiled in Table VI. The accuracy with which the gas evolution curves could be described by this procedure is illustrated in Figure 7, which compares the calculated and observed rates of methane evolution from the Condor carbonaceous shale. However, other cases, e.g., the H_2 evolution from Duaringa shale, were much more complex, and fits of the Anthony Howard equation only to the major contributing processes were attempted.

TABLE V

TOTAL GAS YIELDS TO 850°C[a]

Sample	Gas Yields (cc/g)[b]			
	H_2	CH_4	CO	CO_2
Nagoorin Carbonaceous (16998C)	46.9 (72.2)	19.8 (30.5)	73.5 (113.1)	22.6 (34.7)
Condor Carbonaceous (13338C)	28.0 (100.0)	14.0 (49.5)	17.1 (60.4)	7.3 (58.4)
Condor (19541C)	13.5 (109.7)	3.5 (28.5)	21.3 (173.1)	19.6 (159.3)
Stuart (18313C)	< 1	7.0 (36.2)	16.5 (85.5)	12.9 (66.8)
Duaringa (5363C)	11.4 (102.7)	3.2 (29.0)	5.7 (51.8)	6.9 (62.7)

(a) Heating rate:– 3.0°C/min
(b) At 0°C and 0.1 MPa pressure. Figures in brackets are the gas yields expressed as cc/g of organic carbon.

TABLE VI

SUMMARY OF REPRESENTATIVE PARAMETERS DETERMINED BY FITTING THE ANTHONY-HOWARD EQUATION TO THE RATES OF GAS EVOLUTION

Sample	Gas	Process	Temp. at which rate of process is maximum °C	A S^{-1}	E kJ mol^{-1}	σ (a) kJ mol^{-1}	Fraction (b)
Nagoorin Carbonaceous (16998C)	H_2	1	570	1×10^{17}	318	20	0.14
		2	700		384	31	0.86
	CO_2	1	280	1×10^8	110	8	0.23
		2	400		140	8	0.57
		3	600		182	8	0.20
Condor Carbonaceous (13338C)	CO_2	1	300	1×10^8	120	18	0.40
		2	430		148	6	0.60
	CH_4	1	500	1×10^{15}	256	12	0.36
		2	570		287	14	0.42
		3	700		330	20	0.22
	H_2	1	600	6×10^{15}	297	23	0.26
		2	730		361	29	0.74
Condor (19541C)	CO_2	1	460	5×10^9	178	0.05	1.00
	CH_4	1	500	9×10^{12}	223	10	0.40
		2	580		249	21	0.60
Stuart (18313C)	CO	1	450	5×10^9	174	11	1.00
Duaringa(c) (5363C)	H_2	1	460	1×10^9	165	0.05	1.00

(a) Standard deviation of activation energies.
(b) Fractional contribution of the process considered to the total gas yield.
(c) Only the process with a maximum rate at the indicated temperature was considered in the analysis of the data.

Hydrogen

Examination of the hydrogen evolution profiles shows a striking difference between those observed for the carbonaceous shales and those of the normal shales. For the two carbonaceous shales, hydrogen evolution reaches a maximum in the temperature range 700-720°C with a minor contribution from a process having a maximum of ∿600°C. As summarized in Table VI, the activation energies for the 600°C process are in the range 300-320 kJ mol^{-1}, and 360-380 kJ mol^{-1} for the 700°C process. The hydrogen evolution from these samples thus occurs in a temperature range in which the secondary pyrolysis reactions of the residues which remain after the primary bitumen decomposition is complete are thought to take place (2). In contrast, the hydrogen evolution rates from the Condor and Duaringa deposit resemble those observed for the Green River Shale (2) and show a sharp peak at 460°C, close to the temperature at which the oil formation is maximum. For the Duaringa shale this process is associated with an activation energy of ∿165 kJ mole^{-1} and is followed by further hydrogen evolution obviously comprising many processes occurring in the secondary pyrolysis region.

Methane

The methane evolution profiles for all five shale samples are surprisingly similar, but occur at significantly higher temperatures than have been observed (2) for the Green River shale. Although some methane evolution accompanies the oil formation, the major part is formed in the secondary pyrolysis region. At least three major processes with maxima at 500, 580 and 700°C appear to contribute to the total methane formation. Typical activation energies for these processes were determined for Condor carbonaceous shale and are summarized in Table VI.

Carbon Dioxide

The carbon dioxide evolution profiles for the Nagoorin, Duaringa and Condor carbonaceous shales are characterized by significant contributions commencing at temperatures as low as 150°C. It is unlikely that these processes are the result of mineral decomposition reactions, and their presence must reflect a contribution from thermally very labile components of the kerogen. A further major contribution to the CO_2 yield from these shales was found at temperatures corresponding to the maximum oil formation, but little CO_2 was formed in the secondary pyrolysis temperature range. In this respect, the behavior of these shales differs significantly from the American Green River Shale which shows (2) a negligible CO_2 evolution rate accompanying the oil release, but a very large rate at temperatures above 550°C resulting from the decomposition of the carbonate minerals.

The CO_2 evolution from the Condor and Stuart shales show sharp peaks at 500°C superimposed on a peak corresponding to the temperature at which the oil evolution occurs. These sharp peaks are probably associated with the decomposition of mineral constituents of the shale, but further work with acid washed shales would be required to confirm this conclusion.

Carbon Monoxide

All shale samples showed a significant peak in the CO evolution rates in the temperature range over which oil evolution occurs. At these relatively low temperatures it is unlikely that the reaction between CO_2 and residual char could be a significant source of carbon monoxide (2), and it appears that for these shales and in contrast to the Green River shale (2) the decomposition of the kerogen results in the formation of CO. In the case of the Stuart shale, the processes leading to the formation of the CO in the low temperature range are characterized by a mean activation of ∿174 kJ mol^{-1} and a distribution of 11 kJ mol^{-1} (Table VI).

CONCLUSION

In conclusion, it appears that the shales examined in this study are characterized by the significant evolution of both carbon dioxide and carbon monoxide at temperatures near or below that at which oil evolution occurs. This effect is particularly pronounced for the two carbonaceous shales which also show hydrogen evolution in a temperature range normally associated with secondary pyrolysis reactions. These properties are more characteristic of brown and even bituminous coals, and it is possible that the carbonaceous shales and to a lesser extent the normal shales contain varying proportions of lignin-derived materials in addition to the more conventional oil shale kerogen (11). A detailed comparison of the composition of the oil produced from the carbonaceous and normal shales may provide further confirmation of this hypothesis, as would a petrographic comparison of these materials.
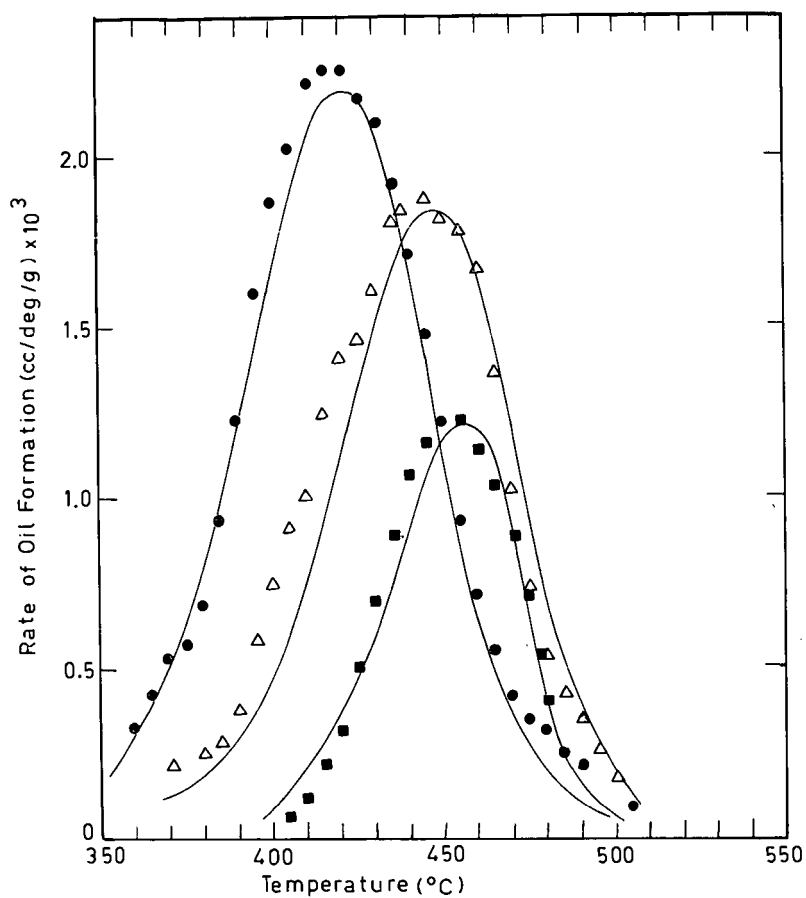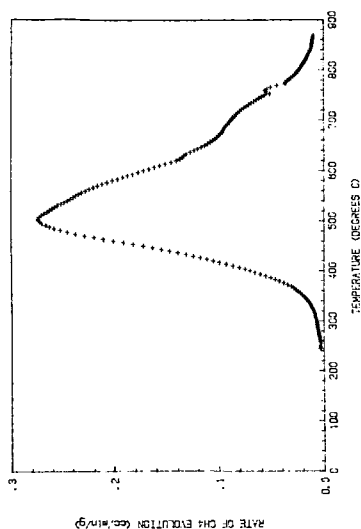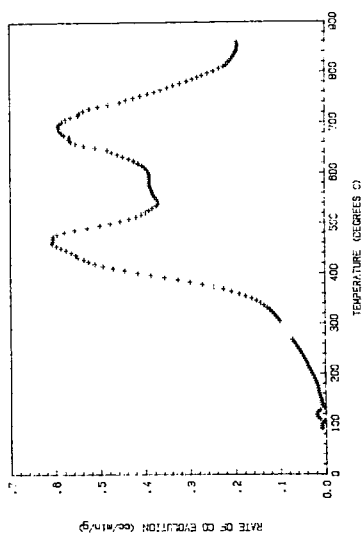
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Figure 1. Effect of temperature on the rate of oil evolution. Heating rate 3°C/min, Argon flow rate 130 cc/min. Points are experimental data, solid line was calculated by Anthony-Howard equation using the parameters summarized in Table IV. ● Nagoorin carbonaceous, △ Stuart, □ Condor carbonaceous.
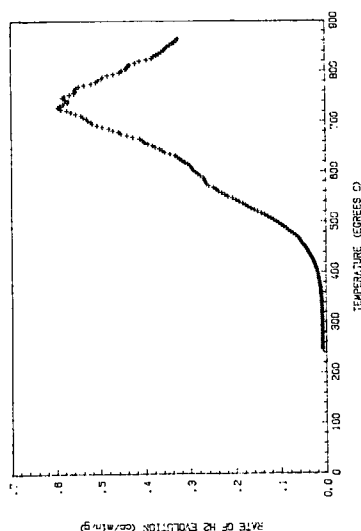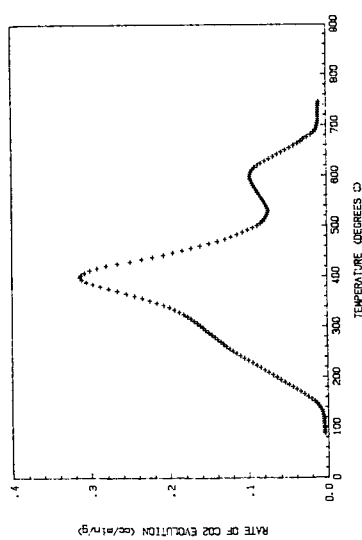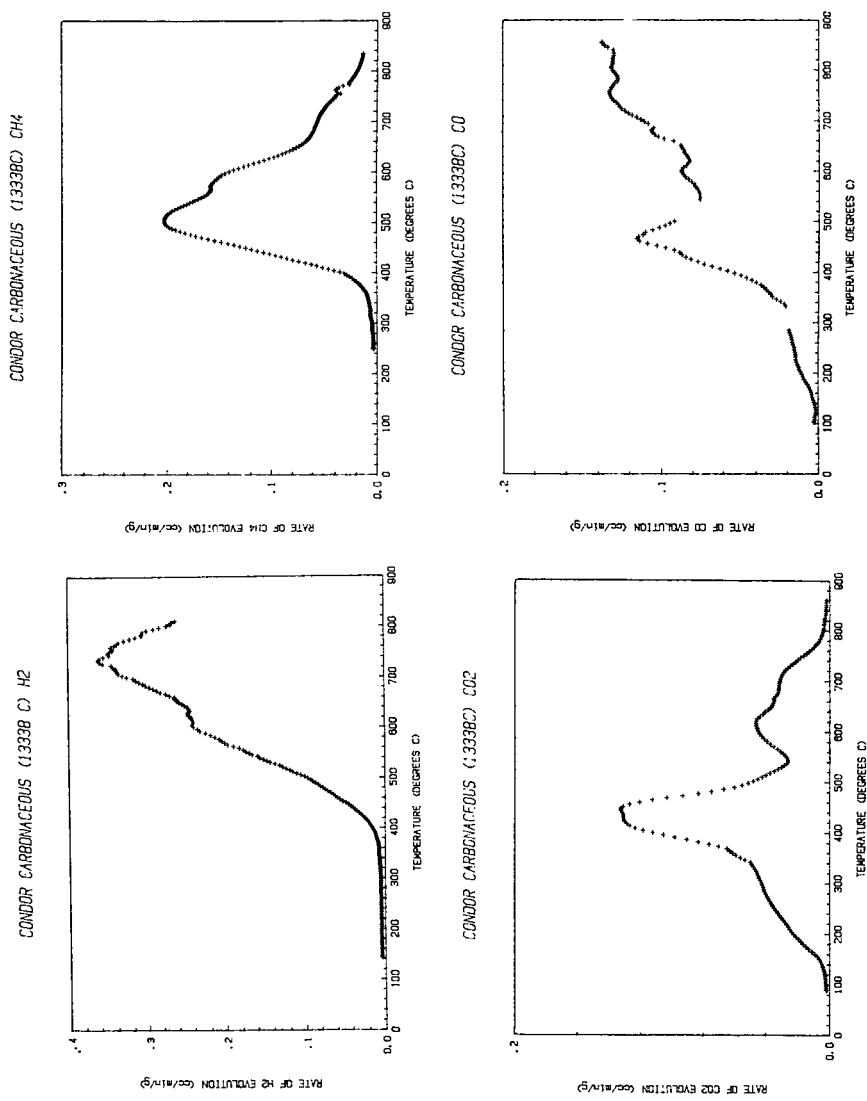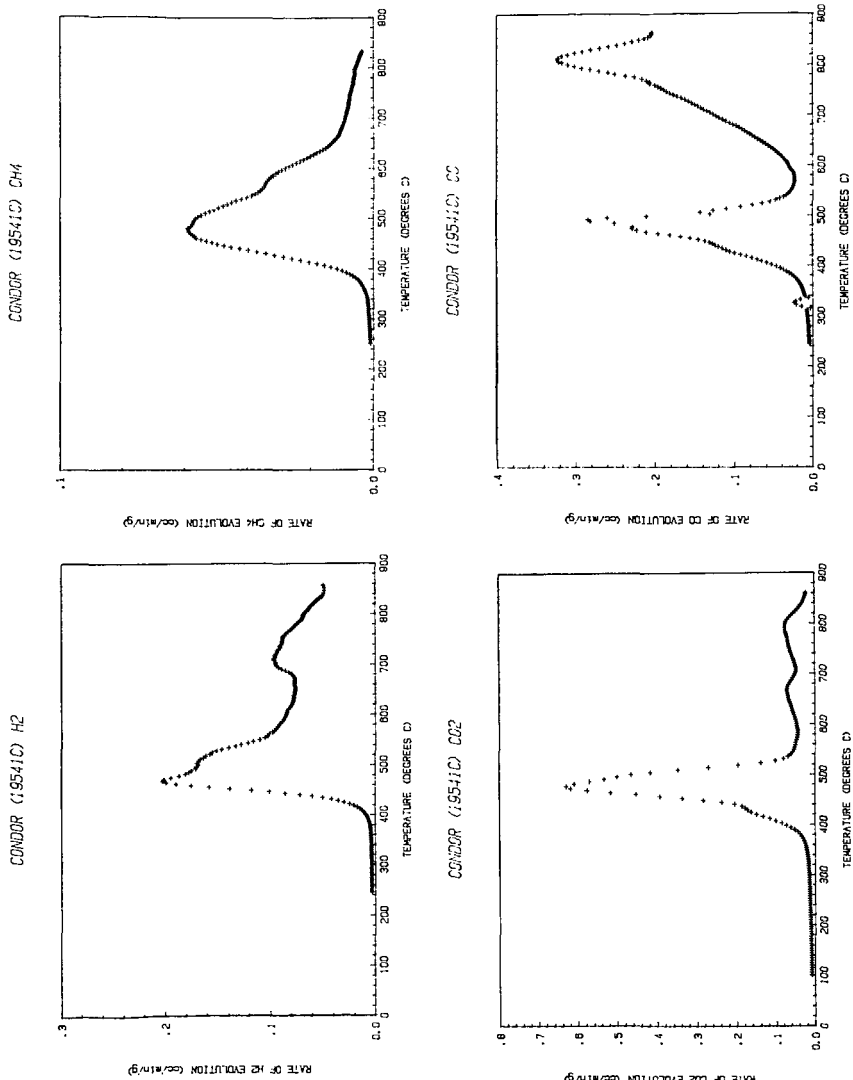
Figure 2. Effect of temperature on the H_2, CH_4, CO_2 and CO evolution rates from Nagoorin shale.

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Figure 3. Effect of temperature on the H_2, CH_4, CO_2 and CO evolution rates from Condor carbonaceous shale.

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Figure 4. Effect of temperature on the H₂, CH₄, CO₂ and CO evolution rates from Condor shale.
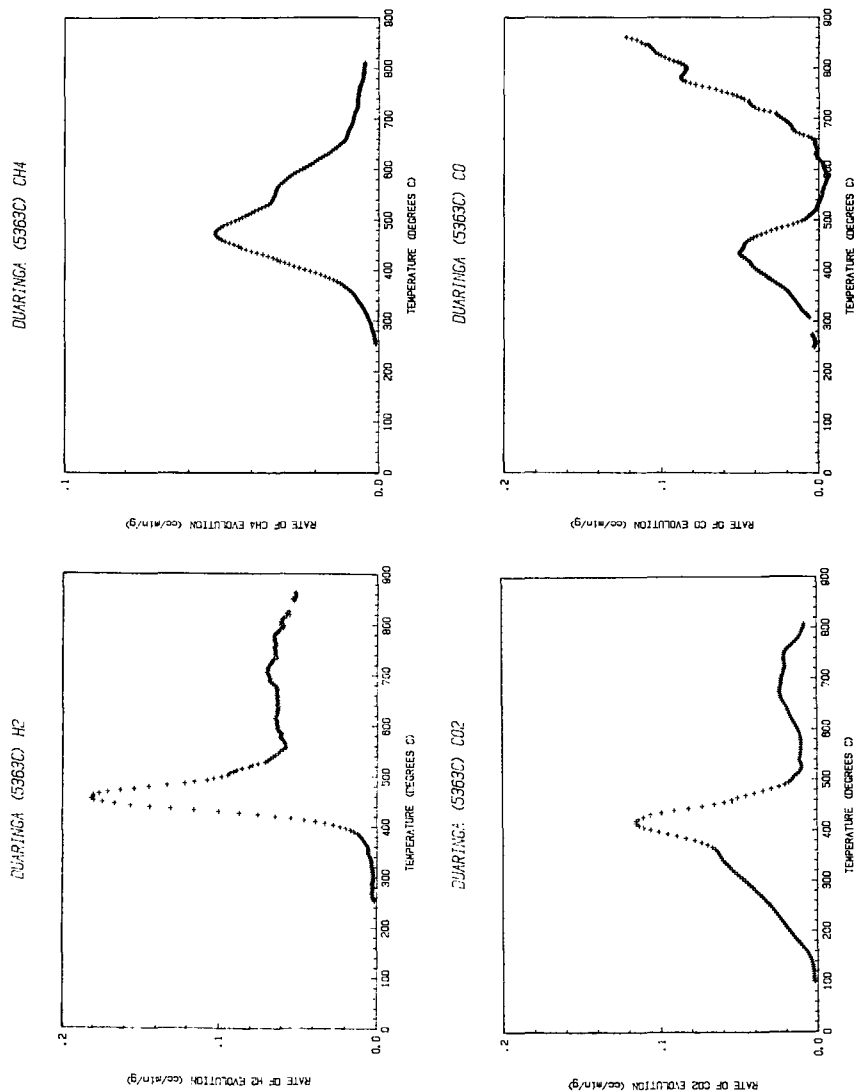
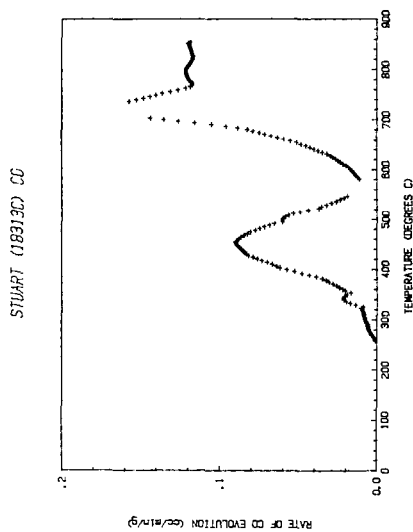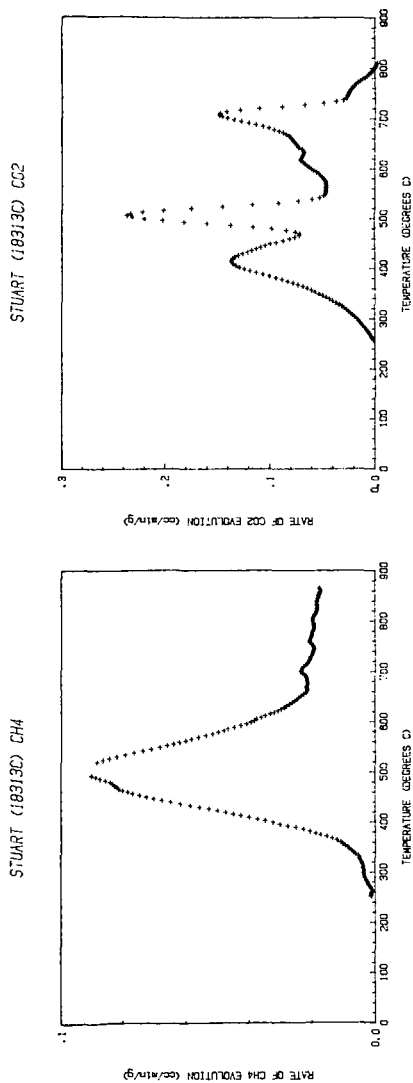Figure 5. Effect of temperature on the H_2, CH_4, CO_2 and CO evolution rates from Duaringa shale.

Figure 6. Effect of temperature on the CH_4, CO_2 and CO evolution rates from Stuart shale.
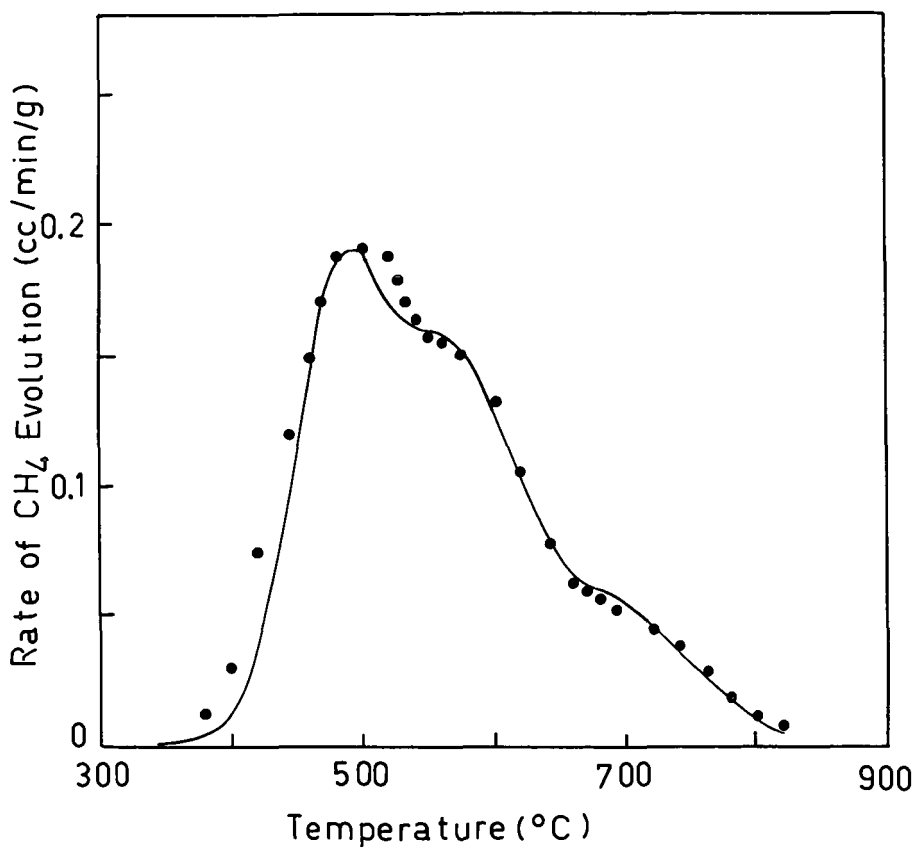
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Figure 7. Comparison of the observed and calculated rate of methane evolution from Condor Carbonaceous shale. Solid line — calculated from Anthony-Howard equation using the parameters summarized in Table XI, ● - experimental data.

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